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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY  
OF HARVARD COLLEGE.

NOTE ON THE CONSTITUTION OF DIPARABROMBENZYL-  
CYANAMIDE.

BY C. LORING JACKSON AND R. W. FULLER.

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THE work described in this paper consists of the conversion of the silver salt of cyanamide into a dialkylcyanamide, and the determination of the constitution of this body. Last summer (after this work was finished) a paper appeared in the "Berichte der deutschen chemischen Gesellschaft," in which Wallach\* described a number of substituted cyanamides obtained by the action of bromide of cyanogen on secondary amines. For fear of approaching too near the field thus reserved by Wallach we shall abandon the further study of dialkylcyanamides, but the study of alkyl compounds of dicyandiamide and dicyanimide will be taken up in this Laboratory; in fact work on this latter substance is already in progress.

Theoretically a dialkylcyanamide derived from the silver salt of cyanamide might have either of the following formulas  $R-N=C=N-R$  or  $R_2N-CN$ , and it is easy to determine by experiment which of these two formulas is correct. So far as we can find, but a single experiment of this sort has been tried; this was published some years ago by Fileti and Robert Schiff,† who prepared diethylcyanamide by the action of ethyl-iodide on argentic cyanamide at  $100^\circ$  for some hours. The product was extracted with ether, and divided into two portions; one was distilled, and gave a boiling point of  $186^\circ$ , whereas Cloez and Cannizzaro,‡ who prepared it by the decomposition of ethyl cyanamide, found a boiling point of  $190^\circ$ . Fileti and R. Schiff analyzed their distillate, and obtained carbon 60.66 instead of 61.22 and hydrogen 10.11 instead of 10.30.

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\* Ber. d. chem. Ges., XXXII. 1872.

† Id., X. 425 (1877).

‡ Ann. Chem., XC. 95.

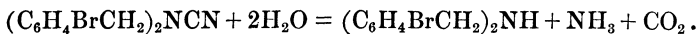
The other portion of their product (which had not been distilled) was decomposed by means of hydrochloric acid on the water bath; the chlorides obtained by evaporating the hydrochloric acid solution were converted into chlorplatينات and crystallized fractionally, when they obtained two end fractions in which the platinum was determined with the following results:—

	$(\text{NH}_4)_2\text{PtCl}_6$	Found.		$((\text{C}_2\text{H}_5)_2\text{NH})_2\text{PtCl}_6$
Platinum	44.04 *	I. 42.51	II. 36.3	35.30 *

$(\text{C}_2\text{H}_5\text{NH}_2)_2\text{PtCl}_6$  requires 39.24 \* per cent of platinum.

In considering these results of Fileti and R. Schiff, it is to be observed that the diethylcyanamide was not purified, and that no very sharp criterion of purity was given (Wallach states that these substances are decomposed by distillation under ordinary pressure, so that the boiling point is not of much value in this respect), further that their analyses of the platinum salts did not give numbers very near to those calculated. It seemed to us, therefore, worth while to try similar experiments with, if possible, a crystalline disubstituted cyanamide, which could therefore be obtained in a state of undoubted purity, and also with one which would yield amines more easily separated than ammonia and diethylamine. We selected for this purpose the diparabrombenzylcyanamide, since the parabrombenzyl compounds show a great tendency to crystallize, and the diparabrombenzylamine, if formed, could be recognized by its melting point,  $50^\circ$  (dibenzylamine is a liquid), while the parabrombenzylamine, if that were the product, gives a carbonate with a definite melting point, and both these amines could be separated without difficulty from ammonia.

The diparabrombenzylcyanamide proved to be a well crystallized solid, melting at  $133^\circ$ . On decomposition with dilute sulphuric acid it gave diparabrombenzylamine, ammonia, and carbonic dioxide by the following reaction:—

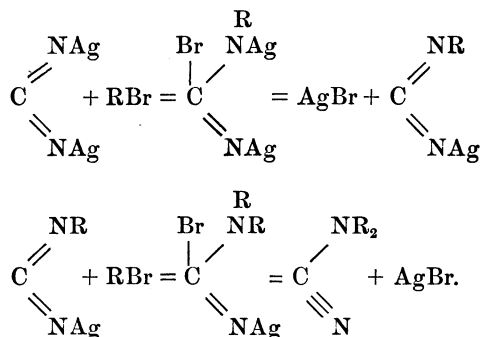


Our results, therefore, confirm those of Fileti and R. Schiff, and leave no doubt that the dialkyl derivatives from argentic cyanamide are cyanamides and not carbodiimides. If they are formed by direct replacement of the silver in argentic cyanamide by the alkyl radicals, the same

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\* These are the numbers given by Fileti and R. Schiff. They would be somewhat altered by using modern atomic weights.

constitution ( $\text{Ag}_2\text{NCN}$ ) must be ascribed to this substance and to cyanamide. If, on the other hand, these compounds are formed by successive additions of the alkyl bromide with splitting off of argentic bromide, the disubstituted cyanamides could be formed from a silver salt with a carbodiimide formula, as is shown by the following reactions:—



Our results, therefore, prove nothing in regard to the true formula of cyanamide.

#### PREPARATION OF DIPARABROMBENZYL CYANAMIDE, $(\text{C}_6\text{H}_4\text{BrCH}_2)_2\text{NCN}$ .

The yellow silver salt of cyanamide,  $\text{Ag}_2\text{NCN}$ , prepared according to Walther,\* was mixed with a benzol solution of parabrombenzylbromide in the proportion of two molecules of the bromide to one of the salt, which should be finely powdered. The mixture was heated in a flask with a return-condenser on the steam-bath, until after four or five hours the full yellow color of the argentic cyanamide had been completely replaced by the yellowish white color of argentic bromide. The precipitate was then filtered out and washed thoroughly with hot benzol, and the filtrate and washings evaporated to dryness, when a thick reddish yellow oil was left. To purify this it was dissolved in hot alcohol, and the strong solution allowed to cool slowly; a yellow oil was deposited at first followed by a white crystalline substance, which was obtained by pouring the solution off from the oil as soon as the crystals began to appear. By repeated recrystallizations of this sort the melting-point of the substance was raised to  $133^\circ$ , where it remained constant. It was dried *in vacuo* and analyzed with the following results:—

\* Journ. prakt. Chem., 1896, 510.

- I. 0.1508 gram of the substance gave by the method of Carius 0.1494 gram of argentic bromide.
- II. 0.3041 gram of the substance gave 20.2 c.c. of nitrogen at a temperature of  $18^{\circ}.6$  and a pressure of 760.4 mm.

	Calculated for ( $C_7H_5Br$ ) <sub>2</sub> NCN	I.	Found.	II.
Bromine	42.11	42.18		
Nitrogen	7.37			7.64

In view of the great tendency of cyanamides to polymerize, it was thought safer to determine the molecular weight of the body \* by the method of freezing a benzol solution, which gave the following results:—

0.375 gram of the substance dissolved in 16.25 grams of benzol produced a depression of  $0^{\circ}.28$  in the freezing point.

	Calculated for ( $C_7H_5Br$ ) <sub>2</sub> NCN.	Found.
Molecular weight	380	337

There can be no doubt, therefore, that the substance is really ( $C_6H_4BrCH_2$ )<sub>2</sub>NCN.

#### PROPERTIES OF DIPARABROMBENZYL CYANAMIDE.

The substance crystallizes from benzol in sheaves of white crystals shaped like the blade of a lancet, sometimes united laterally into groups with comb ends. It melts at  $133^{\circ}$ . It is freely soluble in benzol, chloroform, acetone, or acetic ester; soluble in toluol; slightly soluble in cold ethyl or methyl alcohol or glacial acetic acid, freely soluble in these solvents when they are hot; slightly soluble in ether, carbonic disulphide, or in hot or cold water; essentially insoluble in ligroïne. It is slowly decomposed by cold strong sulphuric acid; apparently unaffected by hydrochloric acid or nitric acid in the cold. The best solvent for it is hot alcohol.

In order to see if it could form a chloride, a portion of the diparabrombenzylcyanamide was dissolved in anhydrous benzol and saturated with dry hydrochloric acid gas. No precipitate was formed even after the mixture had stood for two weeks, and on evaporating off the benzol the original substance was recovered unaltered. It would seem from this experiment that the diparabrombenzylcyanamide cannot unite with hydrochloric acid.

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\* This work was done before the appearance of Wallach's statement that disubstituted cyanamides show no tendency to polymerize.

A number of experiments were tried in the hope of obtaining polymeres of the diparabrombenzylcyanamide. A dilute solution of sodic or potassic hydrate produced no effect on the substance, either by long standing in the cold or by boiling the mixture. The substance was boiled for two weeks with a solution of ammoniac hydrate, care being taken to replace the ammonia which escaped, but the only change observed was that the color turned from white to pale brown, evidently due to a slight decomposition, since the melting point of the substituted cyanamide was essentially unaltered. Water alone was also tried at the boiling point, but produced no change. Upon heating the substance above its melting point it remained unaltered to  $160^{\circ}$ ; above this point it turned first yellow, and at higher temperatures red, and on cooling gave an oily product, which we could not bring into a fit state for analysis. A similar viscous product was obtained when the substance was heated with sodic acetate. In both these cases it seemed evident that a decomposition had taken place rather than a polymerization, and our experiments, therefore, confirm the statement of Wallach that these dialkylcyanamides show no tendency to polymerize.

#### DECOMPOSITION OF DIPARABROMBENZYL CYANAMIDE.

As some preliminary experiments showed that the substituted cyanamide was decomposed with difficulty by hydrochloric acid in open vessels, we adopted a dilute sulphuric acid having a specific gravity of 1.44, which has frequently given good results in this Laboratory. Several grams of the diparabrombenzylcyanamide were boiled with a large excess of this acid in a flask with a return-condenser. Soon after the substance melted in the hot acid an effervescence was observed, and upon testing the gas given off with baryta water, it proved to be carbonic dioxide. As the oily drops did not disappear, the heating was continued for ten hours, which reduced the amount of oil, but did not entirely remove it. On cooling, the whole liquid became filled with a voluminous white crystalline precipitate; we determined, therefore, to stop the process at this point and isolate this crystalline substance, which could be easily separated from the portion undissolved in the hot sulphuric acid. This latter substance which solidified on cooling, seemed to consist of undecomposed diparabrombenzylcyanamide, as it gave a fresh quantity of the crystalline product on boiling again with sulphuric acid; its amount was insignificant. To obtain the crystalline product it was filtered from the acid liquid, washed with a little cold water to free it from adhering acid, and then dissolved in hot water, which left behind the few black lumps of undecomposed cyanamide. The solution was then filtered, and the sul-

phate decomposed by the addition of a strong solution of sodic hydrate, which set free the base as a pasty mass solidifying on cooling. This base, after purification by crystallization from alcohol, showed the constant melting point  $50^{\circ}$ , which is that of the diparabrombenzylamine\*  $(C_6H_4BrCH_2)_2NH$ . For greater security the chlorplatinate was prepared and analyzed. Chlorplatinic acid added to an alcoholic solution of the base gave a yellow precipitate, which was purified by washing with alcohol, and dried *in vacuo*.

0.1783 gram of the salt gave on ignition 0.0309 gram of platinum.

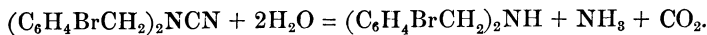
	Calculated for $[(C_6H_4Br)_2NH_2]_2PtCl_6$ ,	Found.
Platinum	17.58	17.34

The sulphuric acid filtrate from the crystals of the diparabrombenzylamine sulphate was treated at first with sodic carbonate, and finally with a large excess of sodic hydrate, and distilled with steam, the distillate being collected in a series of flasks containing hydrochloric acid. After the distillation was finished, the contents of the flasks were evaporated to dryness on the steam bath, and the white residue dissolved in a little water and converted into the chlorplatinate; this was a yellow precipitate crystallizing in octahedra, which was washed with water and alcohol, dried *in vacuo*, and analyzed with the following results:—

0.2061 gram of the chlorplatinate gave on ignition 0.0903 gram of platinum.

	Calculated for $(NH_4)_2PtCl_6$ .	Found.
Platinum	43.91	43.81

It is evident from the experiment described above that the products of the decomposition of diparabrombenzylcyanamide, when boiled with dilute sulphuric acid, are carbonic dioxide, diparabrombenzylamine, and ammonia. The reaction, therefore, runs as follows:—




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\* Jackson, These Proceedings, XVI. 254.